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Dielectric behaviour and charge transfer complexation in ternary liquid mixtures

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Abstract : Dielectric constant measurements for four ternary mixtures, (i) *n*-butylamine + pentanoic acid + benzene, (ii) *n*-butylamine + capric acid + benzene, (iii) *t* butylamine + pentanoic acid + benzene and (iv) *t* -butylamine + capric acid + benzene have been made ad 30, 35 40 and 45°C. The excess dielectric constants of the various ternary mixtures (difference between experimental and ideal mole fraction mixture law values) have been attributed to the formation of charge transfer complexes between the fatty acids and the amines. The decrease in the values of excess dielectric constants, with rise of temperature, has been explained on the basis of disruption of molecular alignments by thermal energy

Keywords : Dielectric constant, viscosity, refractive index

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Dipole moment studies had been undertaken by Sabesan and Vardharajan [1] to study the association complexes of benzaldehyde + phenol in carbontetrachloride. Mishra *et al* [2] studied the charge transfer complexes in binary and ternary systems. They attributed the positive values of interaction dielectric constant to the formation of some new polar species in the solution. Nath and Das[3] have reported the dielectric behaviour of binary and ternary systems containing weakly interacting components at 30°C. The behaviour of donor and acceptor molecules in liquid mixtures is therefore, expected to give an idea about the nature of interaction between the constituents of the mixtures. The dielectric constant measurements have therefore, been employed in this investigations to study the ternary liquid mixtures consisting of the four systems and the effect of temperature on the extent of interactions.

The systems studied in the present investigation are (i) *n*-butylamine + pentanoic acid + benzene, (ii) *n*-butylamine + capric acid + benzene, (iii) *t*-butylamine + pentanoic acid + benzene and (iv) *t*-butylamine + capric acid + benzene.

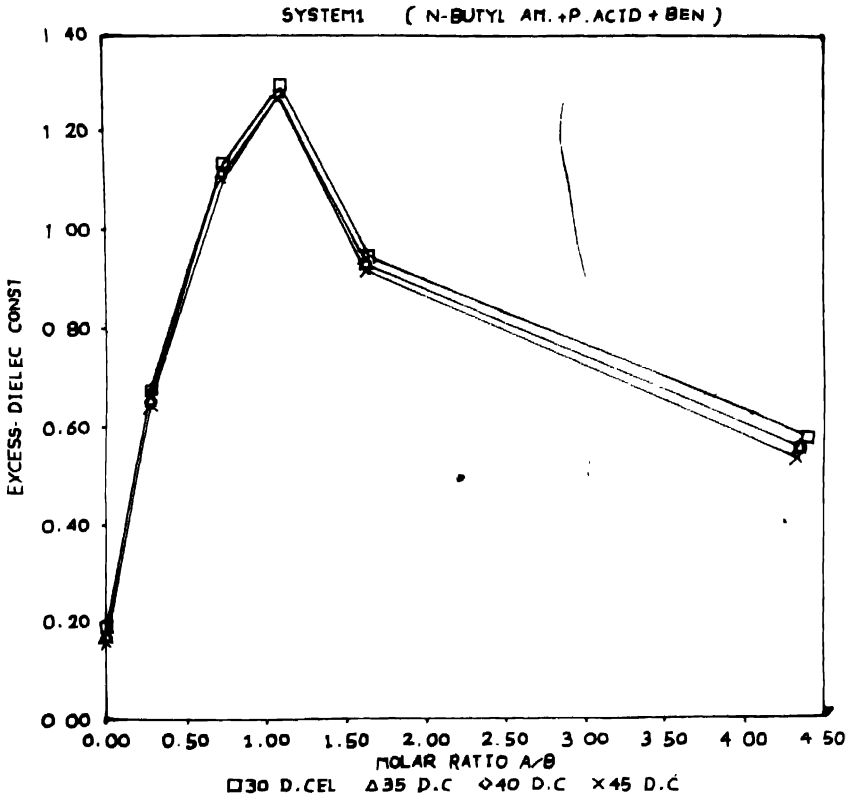

Figure 1. Excess dielectric constants of System 1.

The liquids supplied by MERCK-schuchards, Chemische Fabriek Holland, were used without further purification. The capacitance measurements were made 1 KHz using an LCR-Q-meter supplied by Aplab Autocomput LCR-Q-meter model 4910. The temperature can be kept constant to ± 0.1°. The accuracy in the measurement of dielectric constant was ascertained by comparing the experimental values of dielectric constant of five pure liquids with their literature [4,5,6] values, at the temperature of measurement. The measurements were made at 30, 35, 40 and 45°C.

The values of excess dielectric constants of the four systems at 30°C, 35°C, 40°C and 45°C are plotted in Figures 1, 2, 3 and 4 respectively along with the molar ratio of amine and acid.

The values of excess dielectric constants have been calculated using the relation

$$\Delta\varepsilon_{1,2,3} = \varepsilon_{1,2,3} - \varepsilon_1 X_1 - \varepsilon_2 X_2 - \varepsilon_3 X_3, \quad (1)$$

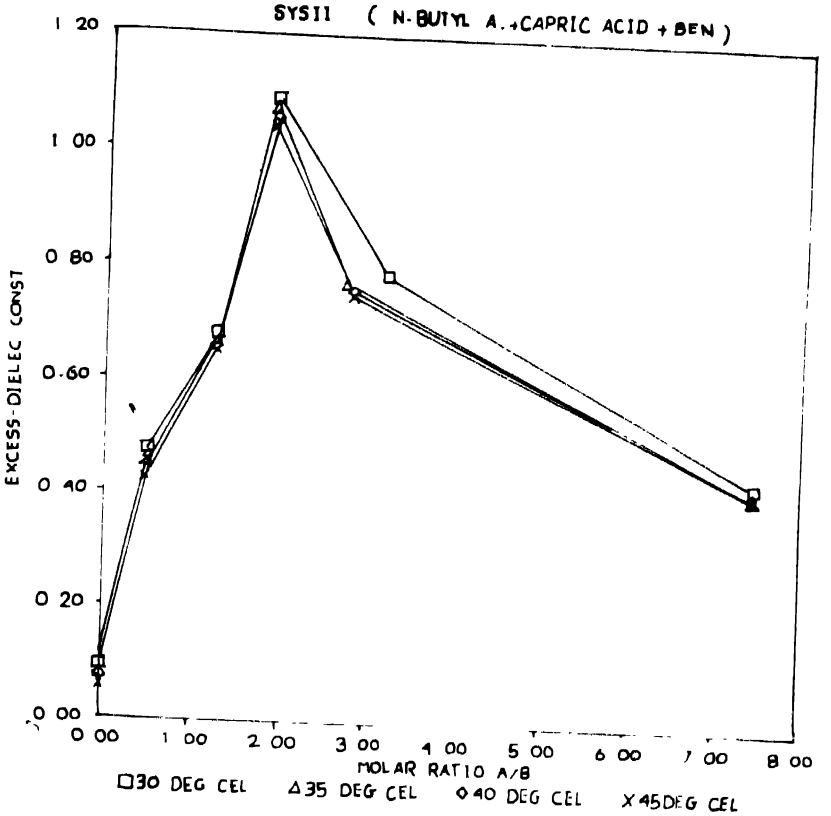

Figure 2. Excess dielectric constants of System II

where ε_1, ε_2, ε_3 and X_1, X_2, X_3 denote the dielectric constants and mole fractions respectively, of the pure components. $\varepsilon_{1,2,3}$ is the dielectric constant of the sample mixture.

The data shown, explicitly brings out the following observations.

1. The excess dielectric constant $\Delta\varepsilon_{123}$ is +ve in case of all the sample mixtures studied and at all the temperatures.
2. The excess dielectric constant follows a particular trend, first it increases, becomes maximum and then decreases again.
3. The maxima of $\Delta\varepsilon_{1,2,3}$ decreases with increase of temperature.

The +ve values of $\Delta\varepsilon_{1,2,3}$ can be attributed to the increase in the alignment of the molecules of the constituent liquids. The maximum of $\Delta\varepsilon_{1,2,3}$ *vs*. molar ratio can possibly be

due to the complex formation between the amines and the acids. The lone pair of electron on the nitrogen of the amine group is always in a readiness to pull the protonic charge. This attraction between the protonic charge and the –ve charge on the N atom, may lead to a complex formation between the acid and the amine, the complexation being of the charge transfer type at the particular molar ratio, corresponding to peak of $\Delta\varepsilon_{1,2,3}$. Further evidence to the formation of such charge transfer complexes in the present case, follows from the observations of Lindemann and Zundel [7] from IR absorption spectra. According to them proton transfer was observed in anhydrous system when the carboxylic acid was more acidic than the nitrogen base by a pka difference of 4. In our case, the pka difference between the acid and amine is greater than 5.

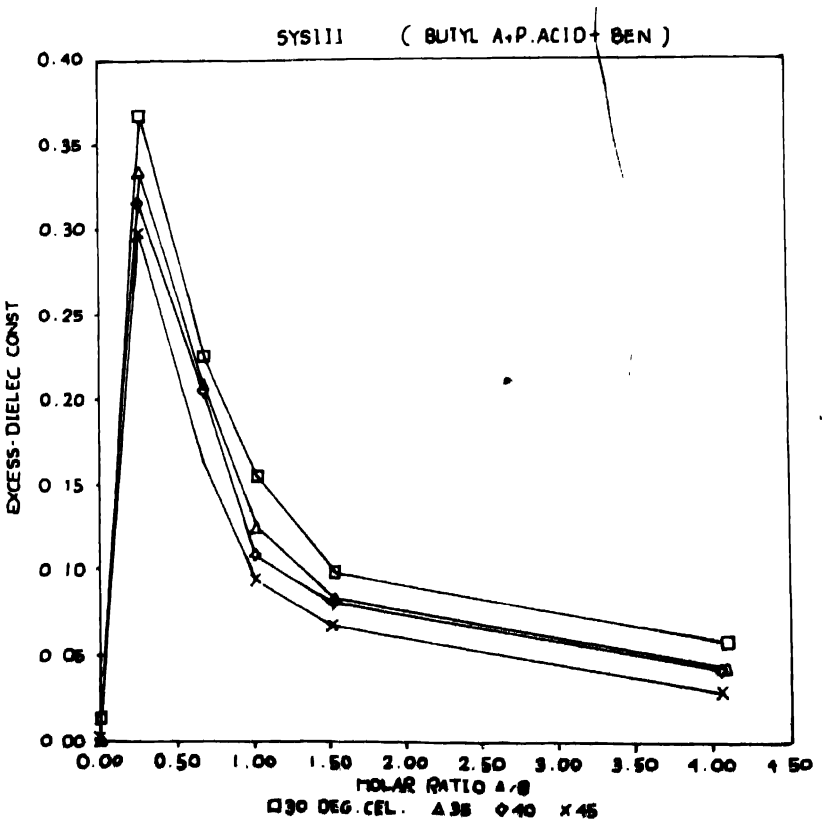

Figure 3. Excess dielectric constants of System III

Further, as the $\Delta\varepsilon_{1,2,3}$ values for each sample mixture are found to decrease with rise of temperature, it follows that the increase in the thermal energy disturbs the process of molecular alignment, thereby resulting in the fall of $\Delta\varepsilon_{1,2,3}$ over the entire composition range.

It can therefore, be concluded that the dielectric constant measurements can predict the formation of charge transfer complexes in ternary mixtures.

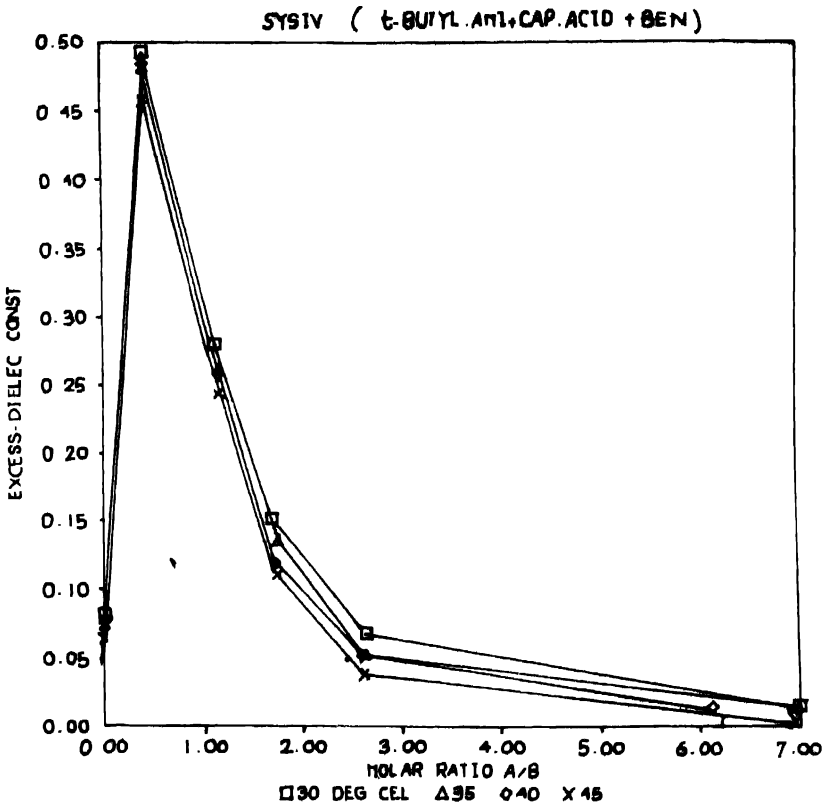

Figure 4. Excess dielectric constants of System IV.

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